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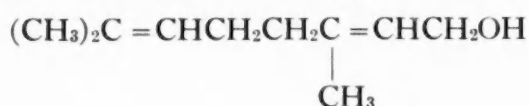
NO. 4

Synthetics Used in Perfumery—Part II

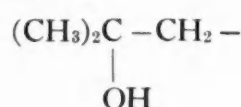
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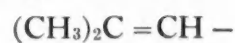
AN interesting group of substances, all of which are related to dimethyloctanol, includes geraniol, citronellol, rhodinol, and linalool, their esters, and the corresponding aldehydes. The first three alcohols and their esters have a rosy odor. Geraniol and citronellol are very closely allied, the former having the formula—



while in citronellol the right-hand double bond is reduced; the completely saturated alcohol is the dimethyloctanol. The well-known citral (lemon) and citronellal (citronella) are the aldehydes corresponding to geraniol and citronellol respectively; hydroxycitronellal has the terminal grouping—



From the formula for geraniol it can be seen that geometrical isomerism is possible at the right-hand double bond. More important, however, is the occurrence of allylic rearrangements at the other ethylene linkage. Thus, the groups—

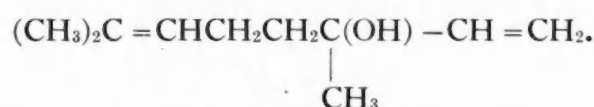


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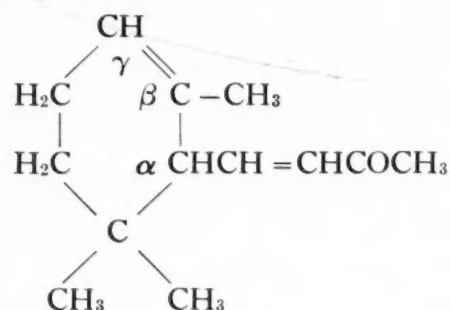
are readily interchangeable and this has caused much controversy in chemical literature. Citronellol and rhodinol,

which have the respective terminal groupings shown, are isomers of this type. Allylic rearrangement of the hydroxyl group is also possible, and accounts for the isomerism of geraniol and linalool, the latter having the formula—



In this series of compounds, the usual replacement reactions do not ordinarily take the expected course. For example, linalool and hydrogen chloride form geranyl chloride rather than the anticipated linalyl chloride.

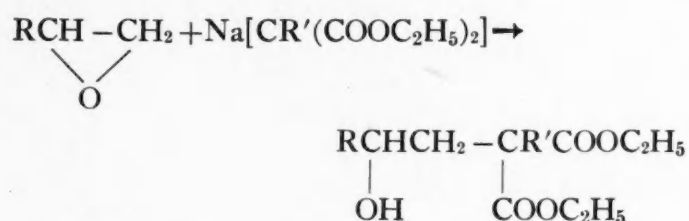
Citral, the aldehyde from geraniol, reacts with acetone to form pseudo-ionone, which in turn may be readily cyclicized to produce a mixture of alpha and beta ionones, the important violet perfumes. The formula below, which has a β,γ -double bond, is that of α -ionone, while in β -ionone the double bond is in the α,β -position.



The substitution of methyl ethyl ketone for acetone results in the methyl ionones. Irone is a naturally occurring

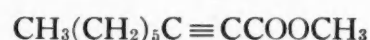
ketone of similar odor and contains a 7-membered ring, but its constitution has not yet been definitely determined.

The lactones, which were mentioned in Part I of this review (SYNTHETIC ORGANIC CHEMICALS, Vol. XI, No. 3, Sept., 1938), are an interesting class of substances that has been rather neglected. The synthesis of branched chain members by ring closure has already been discussed. Undecalactone, which has long been known, is formed by a similar intramolecular ring closure starting with ω -undecylenic acid, the double bond shifting along the chain to the required β, γ -position. It has been erroneously called "aldehyde C_{14} "; the true C_{14} aldehyde (myristic) is now available. A second method of synthesis for preparing branched chain lactones employs alkylene oxides, and is a variation of the malonic ester synthesis—



hydrolysis, decarboxylation, and loss of water finally result in the formation of the lactone. Many lactones, of which cumarin is a familiar example, have pleasant odors.

A great many miscellaneous substances are used in perfumery, among which may be mentioned β -bromostyrene, indole, and the various quinolines; the latter may be reduced, or methylated and then reduced, and are used in small quantities in some of the more modern perfumes. Methyl heptyne carbonate—



imparts a freshness or leafy note to violet perfumes. The corresponding octyne and decyne esters are also employed.

The musks may be divided into two classes—the first consists of the nitrated aromatic substances, and the second, the many-membered ring systems. The latter group is further subdivided into

compounds having odors resembling musk and civet; chemically, these are ketones, esters, and lactones, and are relatively expensive.

The nitromusks, constituting the first group, which are in current use, include musk xylene (2,4,6-trinitro-*t*-butyl-m-xylene), musk ketone (3,5-dinitro-2,4-dimethyl-6-*t*-butylacetophenone), musk ambrette (2,4-dinitro-3-methyl-6-*t*-butylanisole), moskene (probably 3-*t*-butyl-2,6-dinitro-*p*-cymene), and the nitrals which are nitrated analogs of benzaldehyde. To these should be added the recently patented 4,6-dinitro-2,3,5-trimethyl-*t*-butylbenzene.

The second class, those consisting of many-membered ring systems, is associated with the brilliant work of Ruzicka in identifying and synthesizing these compounds. Included in this group are the ketones, cyclopentadecanone (Exaltone) and its β -methyl homolog which is the naturally occurring muskone recently synthesized by Ziegler; the esters, tetradecamethylene carbonate and ethylene brassylate (Astrotones); and ambrettole. The last is the lactone corresponding to cyclopentadecanone and is obtained from it by oxidation with Caro's acid (H_2SO_5).

It appears that nearly all of the ring systems having 14-16 members, mostly carbon, have a musklike odor, whereas the civet quality prevails in those having 17 members. The presence of oxygen is unnecessary, for cyclic imines have the same musklike odor; however, two oxygen atoms connected by ether linkages may equally well be present.

Two general procedures are used for the formation of large rings—the high dilution method and the radical interchange method. In the former, the reaction is carried out in such a way that only a few molecules are in the mixture at a given moment; consequently, it is more probable that each will react with itself rather than with another molecule. By this procedure, lactones and ketones are secured, the ketones being obtained

by hydrolysis and decarboxylation of the iminonitriles formed from α - ω -dinitriles (Ziegler's procedure).

The radical interchange method is used for securing esters; it consists essentially of the formation of a high poly-

mer from a polymethylene glycol and ethyl carbonate, with subsequent depolymerization in a molecular still.

These new musks are readily obtainable in a pure state, thus facilitating their use in perfume formulas.

Eastman Organic Chemicals as Analytical Reagents

XLVIII REAGENTS FOR ZIRCONIUM

n-PROPYLARSONIC ACID

Geist and Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **9**, 169 (1937)

This reagent is suitable for the determination of zirconium in steels, even for amounts as low as 0.1% and in the presence of many other metals. After the usual procedure of evaporation of the solution, dehydration of the residue and extraction with acidified water, an aqueous solution of n-propylarsonic acid is added to precipitate zirconium. Reprecipitation avoids interference from iron. The residue is ignited and weighed as zirconium dioxide. Tin in the residue is removed by addition of ammonium iodide and reignition.

p-DIMETHYLAMINOAZOPHENYLARSINIC ACID

Feigl, Krumholz, and Rajmann, *Mikrochemie*, **9**, 395 (1931)

The zirconium salt of p-dimethylaminoazophenylarsinic acid forms in acid solution as a brown precipitate. When used as a spot test on filter paper, the precipitate stays in the pores as a characteristic lake color, while the excess reagent can be washed out with dilute acid. Interfering metals can be removed by treating the spot with hydrochloric acid.

β -NITROSO- α -NAPHTHOL

Bellucci and Savoia, *Chem. Zentr.*, **1**, 2531 (1924)

When a 2% alcoholic solution of β -nitroso- α -naphthol is added to a hydrochloric acid solution of zirconium, a deep red color with no precipitation results; precipitation takes place only with the addition of sodium acetate. If a drop of

the acid test solution is placed on filter paper which has been impregnated with an alcoholic solution of β -nitroso- α -naphthol and dried, a more or less deep red fleck forms on the yellow-brown paper when zirconium is present. Large quantities of fluorides or sulfates interfere, but the latter can be eliminated with barium chloride.

CUPFERRON

8-HYDROXYQUINOLINE

Tzinberg, *Zavodskaya Lab.*, **4**, 735 (1935)

The determination of zirconium in ferrozirconium is based on the solubility of zirconium hydroxyquinolate in dilute acetic acid. The sample is decomposed in nitric and hydrofluoric acids, the solution evaporated with sulfuric acid, and the residue dissolved in hydrochloric acid. The iron is precipitated by 8-hydroxyquinoline in the presence of tartaric acid and acetic acid. The zirconium, which remains in the filtrate, is precipitated by cupferron, and ignited to ZrO_2 .

ALIZARIN

de Boer, *Chem. Weekblad*, **21**, 404 (1924)

Zirconium salts in acid solution form a red-brown to dark violet precipitate upon the addition of an alcoholic solution of alizarin. A drop of the test solution, which should be as nearly neutral as possible, is placed in a crucible with a drop of the alizarin solution. The mixture is boiled once, whereupon a red to violet coloration forms if zirconium, beryllium, aluminum, titanium, or thorium is present. The addition of a drop of dilute hydrochloric acid removes the color, except in the presence of zirconium.

Tests Prove the Quality



IN the preparation of organic chemicals, one of the very important stages, from the standpoint of the consumer, is the testing. The above illustration shows a portion of the Testing Laboratory where all Eastman Organic Chemicals are carefully checked and inspected.

All compounds must come into this department for analysis before they can be placed in stock. It is here that the high quality and uniformity characteristic of Eastman Organic Chemicals are safeguarded. Melting points, boiling

points, and other fundamental constants are accurately checked to determine whether or not they comply with the strict Eastman standards. If a chemical fails to meet any requirement, it is promptly rejected; only those that measure up to all specifications of quality reach the stockroom.

The equipment shown includes apparatus for the determination of boiling points and distillation ranges, three different types of equipment for obtaining melting points, and a refractometer.